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Green Nanochemistry Approach to Titanium Dioxide Nanoparticle, Dye-Sensitized Solar Cells

by Hailey E. Cramer, Mark H. Griep, Daniel S. Choi, and Shashi P. Karna

ARL-TR-6033 **June 2012**

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Hailey E. Cramer
University of Delaware

Mark H. Griep
National Research Council

Daniel S. Choi
Georgetown University

Shashi P. Karna
Weapons and Materials Research Directorate, ARL

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[*]University of Delaware, Newark, DE 19716

[†]National Research Council, Postdoctoral Fellow, 500 Fifth St. NW, Washington, DC 20001

[‡]University of Georgetown, Washington, DC 20057

14. ABSTRACT

Dye-sensitized solar cells (DSSCs) are a class of thin-film solar cells which can be created using low-cost materials and natural dyes. They have the potential to achieve comparable efficiency to bulky silicon photovoltaic cells, while providing many other distinct advantages such as a more tunable band gap and device flexibility. In this research, anthocyanin, a natural dye extracted from various fruits, was used and tested as the photon harvesting/electron donating dye in titanium dioxide nanoparticle-based DSSCs. Anthocyanin molecules were extracted through mechanical pulverization and chemical extraction methods, with both being evaluated in a DSSC system. These results demonstrate that DSSCs made from chemically extracted blackberry-based anthocyanin cells produced almost 5× greater photocurrent density compared to DSSCs made through the mechanical pulverization method. The highest output was achieved with DSSCs created through the use of chemically extracted blueberry anthocyanin dyes, producing a photocurrent density, *I*sc, of 7.30 mA and an open circuit voltage, *V*oc, of 335 mV.

15. SUBJECT TERMS

dye-sensitized solar cells, anthocyanin, natural dyes, DSSCs

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1. Introduction and Background

The sun has been used as a source of energy since ancient times. Roman architecture often implemented south-facing glass windows to harness the sun's energy to heat homes. Native Americans built their houses on the sides of hills in order to heat their homes during the day and release heat at night. Although solar power has been used, though passively, by humans since almost 400 BC, it was not until the 19th century that solar power could be collected and converted to electricity through a photovoltaic cell. Since the development of commercially viable silicon-based solar cell technology in the early 1950s, solar power research has continued to grow into first- and second-generation silicon solar cell technologies, which are commonly used today. New research into third-generation solar cells has just begun. These technologies include polymer-based solar cells, nanocrystalline cells, and dye-sensitized solar cells (DSSCs).

DSSCs have gained recent attention as a potential alternative to silicon solar cells due to their low cost, ease of manufacturing, tunability, and robustness/flexibility. They are not inherently brittle, as with silicon-based technologies, and do not have to be positioned at a specific angle of incidence. They can also be engineered to be flexible, which would allow roll-by-roll manufacturing. In 1991, Michael Grätzel and colleagues introduced the use of titanium dioxide (TiO_2) nanoparticles in DSSCs to increase the cell's efficiency (*1*). Recently, titania nanotubes have also been used in DSSCs for efficient electron collection (*2*). The titania nanostructures create a porous surface, which yields an abundance of surface area and allows light-harvesting dyes to be easily absorbed. When light is shined on the transparent electrode of the DSSC, the electrons in the highest occupied molecular orbitals (HOMO) in the dye molecules are excited to the lowest unoccupied molecular orbitals. These HOMOs eventually move to the close-lying state of TiO_2 nanoparticles and are transported to the electrode. An I^-/I_3^- is used as a redox couple to replenish electrons to the dye molecules, thus creating a circuit. The photon-to-electron conversion process is more extensive compared to silicon solar cells. The dyes and electrolyte solution degrade over time, which makes DSSCs less efficient than silicon solar cells. However, the disadvantages of DSSCs are continually being addressed, allowing DSSCs to reach their potential as a cost-efficient alternative to silicon-based solar cells.

A variety of dyes ranging from ruthenium-based dyes to natural dyes has been applied in DSSC systems (*3, 4*). Ruthenium dyes have been shown to produce up to 10% efficiency but they are costly and toxic. Anthocyanin dyes have been of recent interest to nanobio research because of their ability to absorb light and convert it into electrons in a natural and inexpensive way (*5*). Anthocyanin dyes are also powerful antioxidants and have many health benefits including removal of toxic free radicals from the body. As seen in figure 1, anthocyanin is a highly conjugated ring molecule, facilitating the movement of electrons through its structure.

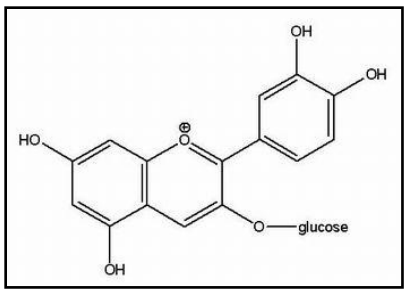

Figure 1. Anthocyanin molecule.

Anthocyanin, which belongs to the class of flavonoids, is commonly found in tissues of many different fruits and plants. In cell vacuoles, anthocyanins absorb light in the blue-green region between the 450- and 600-nm wavelengths; this allows many fruits and plants to reflect red, purple, or blue. Depending on the type of anthocyanin, pH, the sugar attached, and where the sugar is located on the anthocyanin molecule structure, the anthocyanin molecule will absorb different ultraviolet-visible wavelengths. In this work, we focus on the relative photon-to-electron conversion efficiency of fruit-based anthocyanin sources. Specifically, this work focuses on comparing the relative efficiencies of TiO_2 nanoparticle-based DSSCs utilizing anthocyanin dyes extracted from blackberries and blueberries.

2. Materials and Experimental Procedure

The DSSCs used in this experiment were composed of a fluorine-doped, tin-oxide (FTO)-coated glass substrate, which was coated with a thin layer of TiO_2 nanoparticles to which anthocyanin dye had been absorbed. A platinum-coated glass plate was used as a counter electrode, and an iodide/triiodide (I^-/I_3) electrolyte solution was placed between the plates.

2.1 TiO_2 Nanoparticle Substrate Preparation

In synthesis of a TiO_2 nanoparticle solution, the solvent used, the viscosity and uniformity of the solution, and the thickness of the solution layer were considered. Different deposition techniques including spray deposition, spin coating, and doctor blading were considered. The easiest and most effective method for creating a crack-free and anatase layer of TiO_2 nanoparticles was the following: 2.00 g of titanium dioxide nanopowder (Sigma Aldrich, <25 nm 99.7% metal basis) was slowly added to 3.20 mL of a 10% solution of acetic acid on a magnetic hot plate set at 80° C and mixed with a magnetic stir bar. After heating, 200 µL of ethyl alcohol was added to improve the viscosity of the solution. The solution was then sonicated for 20 min, and 300-µL polyethylene glycol (MW = 200) was added to improve porosity. The solution was heated again for 10 min, sonicated for 15 min, and allowed to stir overnight in order to create a uniform solution.

The TiO_2 solution was deposited using the doctor blading method in which the conductive sides of 2.54- × 2.54-cm FTO glass substrates were taped with Scotch* tape about 5 mm from the edge on two opposing sides. The doctor blading method created a 40–50-µm trough in which the TiO_2 solution was spread using a glass slide to create a thin even layer. The Scotch tape was then removed, and the TiO_2 substrates were allowed to air dry for 10 min. The substrates were then annealed at 450° C for 30 min, with a ramp speed of 20° C/min to achieve the anatase crystal phase (*6*). An annealed photoanode before dye absorption can be seen in figure 2.

Figure 2. Annealed photoanode.

2.2 Anthocyanin Dye Extraction

In previous studies, anthocyanin dyes were extracted according to a mechanical pulverization method to produce a crude extract (*7*). This method was reproduced in this experiment. However, in addition to mechanical extraction, a chemical extraction method was utilized to produce a purified anthocyanin extract. In the mechanical extraction method, blackberries and blueberries were crushed to expose natural dyes using a mortar and pestle. In the chemical extraction method, anthocyanin dye from blackberries and blueberries was extracted as follows: Fruits were blended into a slurry mixture, and 200 mL of each juice was poured into a Nalgene† bottle. The bottles were then placed into liquid N_2 and allowed to freeze for 3 h. After freezing, the frozen fruit juices were scraped out of each bottle and ground using a mortar and pestle. While continuing to grind the fruits, 40 mL of a methanol 1% 1.0 M HCl solution was poured onto each fruit sample (80 mL methanol, 80 µL of 1.0 HCl). Extraction of anthocyanin dye was then allowed to occur overnight in a refrigerator. Following refrigeration, the blackberry and blueberry solutions were poured into several 50-mL centrifuge tubes to the 30-mL line. Under a fume hood, 4-mL distilled H_2O and 10-mL chloroform was added to each centrifuge tube. The fruit samples were then centrifuged at 8000 rpm for 10 min. The supernatant was extracted under a fume hood, and each tube was supplemented with 8 mL of a 60% methanol–1% HCl–40% distilled H_2O solution.

* Scotch tape is a registered trademark of 3M Company.

† Nalgene is registered trademark of Nalge Nunc International Corporation.

The crude extract (mechanical pulverization) produced a slurry mixture, while the purified extract (chemical extraction) produced a clear and uniform solution. The difference in the crude and pure blackberry anthocyanin can be observed in figures 3a and b, respectively.

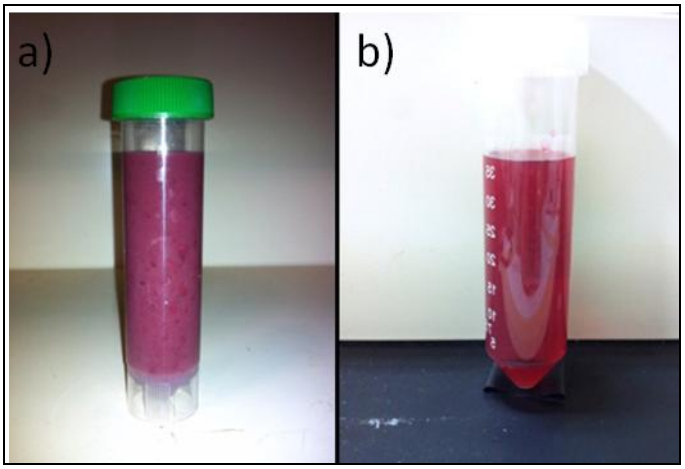

Figure 3. (a) Crude anthocyanin and (b) purified anthocyanin.

2.3 DSSC Assembly

Annealed TiO_2 nanoparticle photoanodes were placed into each dye solution (crude and purified) to allow the dyes to absorb on the TiO_2 surface overnight. Once the dyes were absorbed, as seen in figure 4, each photoanode was washed with ethanol to remove excess dye and the sample was dried with nitrogen. The TiO_2 surface was scraped off around the edges to create a 1- × 1-cm square in the bottom center of each photoanode using a razor blade. Double-sided Kapton‡ tape was placed around the square and copper tape was placed onto the conductive side of the glass on one end. Each photoanode was then placed face down onto the conductive side of a platinum-coated counter electrode to which copper tape had been applied as well. The platinum counter electrodes were created by sputtering platinum onto FTO coated glass substrates to create a platinum thin film of about 50 nm. Two 1 mm diameter holes were drilled into the counter electrode to allow electrolyte to be added and for air to escape. The two plates were sealed together and 15 µL of an I^-/I_3 electrolyte solution was pipetted into the holes in the platinum counter electrode. An additional piece of Kapton tape was placed over the holes to avoid leakage. The I^-/I_3 was prepared by mixing 3.346 g LiI, 634.522 mg I_2, and 4.056 g 4-tert-butylpyridine in 50 mL acetonitrile. A deconstructed DSSC (before sealing platinum counter electrode and photoanode together) and a constructed DSSC (completed DSSC with electrolyte) can be seen below in figures 5a and b, respectively.

‡Kapton is a registered trademark of E.I. duPont de Nemours and Company.

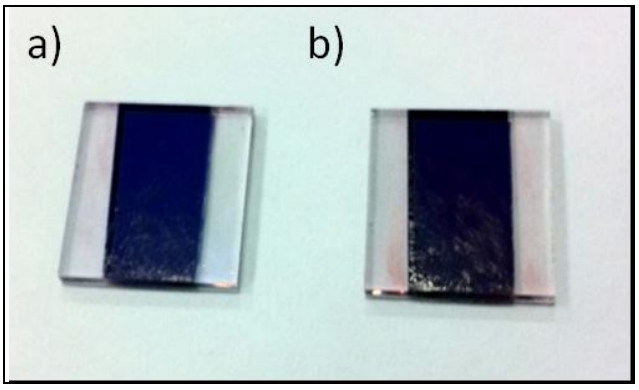

Figure 4. Pure (a) blackberry and (b) blueberry DSSCs.

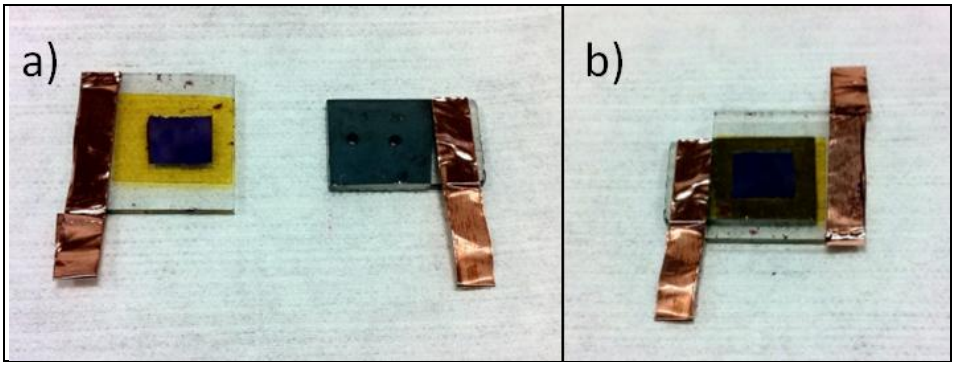

Figure 5. (a) DSSC photoanode and platinum counter electrode and (b) completed DSSC.

2.4 DSSC Photovoltaic Measurement

Current-voltage (I-V) measurements were taken and analyzed with a Keithley 6430 semiconductor analyzer unit and LabVIEW program. A piece of electrical tape to which a 0.5- × 0.5-cm square had been cut out was placed onto the DSSC to expose only a 0.25 cm^2 area to allow for consistent testing between samples. During testing, a 100-W Xenon light source was set to 100 mW and shined on the DSSC in ambient lighting. The overall efficiency (n) of the DSSC was calculated from the integral photocurrent density (i_{ph}), the open-circuit voltage (V_{oc}), the fill factor (FF), and the intensity of the incident light (I_s), as shown in equation 1. The I-V measurement setup can be seen in figure 6.

$$n = \frac{i_{ph} \times V_{oc} \times FF}{I_s} \quad . \tag{1}$$

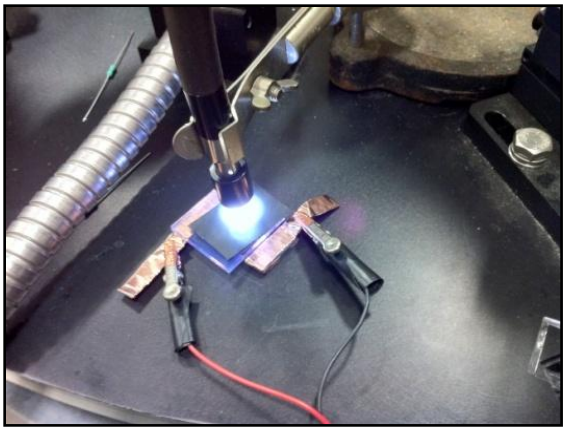

Figure 6. DSSC I-V measurement setup.

3. Results and Discussion

Functional DSSCs were created utilizing two different natural anthocyanin sources. The photoanode topology was analyzed by atomic force microscopy to reveal a porous structure with an average roughness less than 200 nm, as shown in figure 7a. A scanning electron microscopic image, shown in figure 7b, confirmed a continuous anatase TiO_2 nanoparticle film about 15 µm thick.

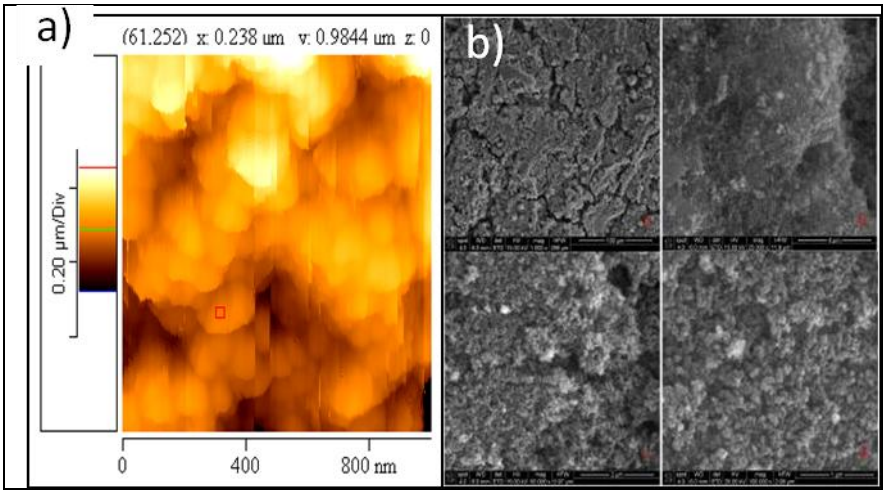

Figure 7. (a) Atomic force microscopy image of TiO_2 surface and (b) scanning electron microscopy image of TiO_2 surface.

Electrical I-V measurements of the DSSCs were measured with a Keithley 6430 semiconductor analyzer unit to determine the DSSC efficiencies. Figure 8 shows the measured I-V curves of the DSSCs using the crude anthocyanin dyes. The current density (mA/cm^2) is shown on the y-axis and voltage on the x-axis. The crude blueberry-based DSSC did not produce an I-V curve typical of solar cells, so the data was not graphed and the efficiency and fill factor could not be reported. The figure shows that the crude blackberry-based DSSC generated a current density of about 1.25 mA/cm^2. After running an I-V sweep, the data was used to calculate the efficiency and fill factor of the DSSCs. The calculated values of the crude blackberry-based DSSC can be seen in table 1.

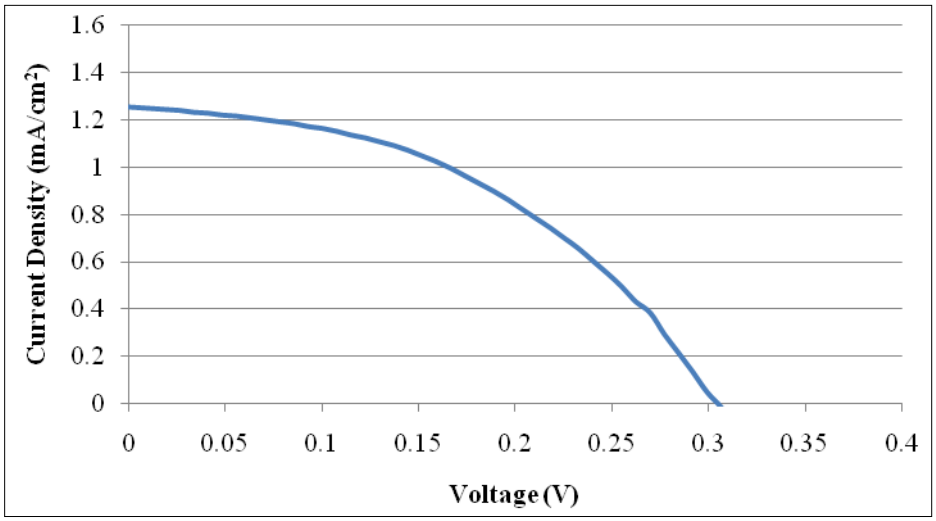

Figure 8. I-V curve of crude blackberry-based DSSC.

Table 1. DSSC efficiency values and calculations.

Dye	Efficiency (%)	Fill Factor (%)	Photocurrent Density (mA/cm^2)	Open-Circuit Voltage (mV)
Crude blackberry	0.15	39.80	1.25	299
Pure blackberry	0.70	37.30	5.61	335
Pure blueberry	0.68	28.00	7.30	335

The I-V measurements of the DSSCs created by using anthocyanin dyes extracted in accordance with the chemical extraction method were also analyzed on the Keithley 6430 semiconductor analyzer unit using a 100 mW/cm^2 input power. The measured I-V curve of the purified blackberry and blueberry anthocyanin DSSCs can be seen in figure 9. The purified blackberry-based DSSC was found to produce almost 5× greater *I*sc compared to the crude blackberry-based DSSC. The purified blueberry-based DSSC was also found to produce an I-V curve. The pure blackberry- and blueberry-based DSSCs generated current densities of about 5.61 mA/cm^2 and 7.30 mA/cm^2, respectively. Calculated values of the purified DSSCs can be seen in table 1.

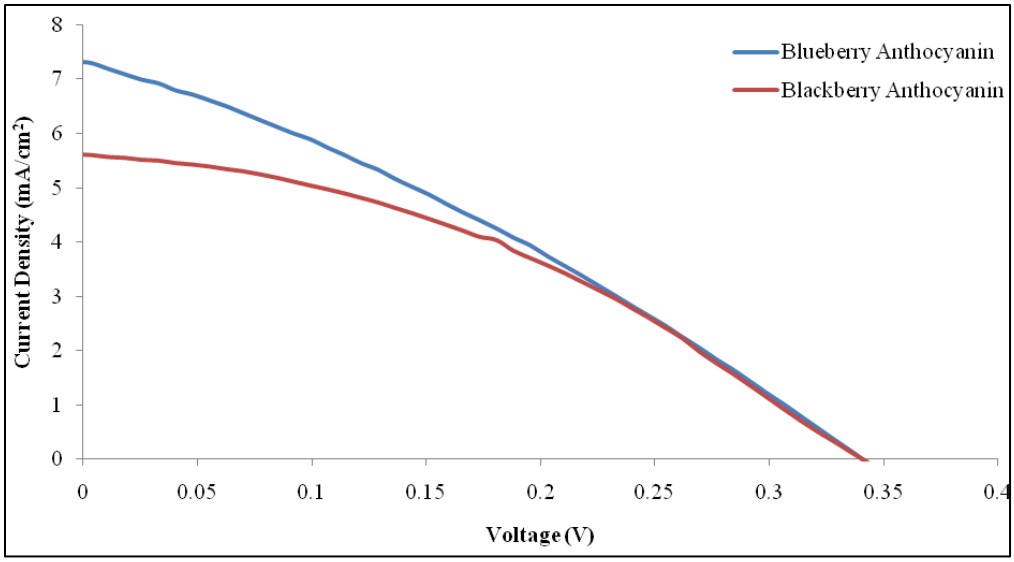

Figure 9. I-V curves of pure anthocyanin DSSCs.

In order to compare the relative merits of the DSSCs created with the use of natural anthocyanin dyes to silicon solar cells, a silicon photovoltaic cell taken from a solar-powered calculator (4-in series) with a total illumination area of 2.5 cm^2 was also analyzed. The I-V curve for the silicon solar cell, along with the measured I-V curves of the purified blackberry and crude anthocyanin DSSCs, is shown in figure 10. The data for the crude and purified blackberry anthocyanin was also extrapolated for 10 DSSCs in a series in order to give a comparable illumination area of 2.5 cm^2. If extrapolated into a series of 10, the purified blackberry DSSC could theoretically produce almost 22× greater *I*sc compared to the crude blackberry-based DSSC, as well as a comparable *V*oc.

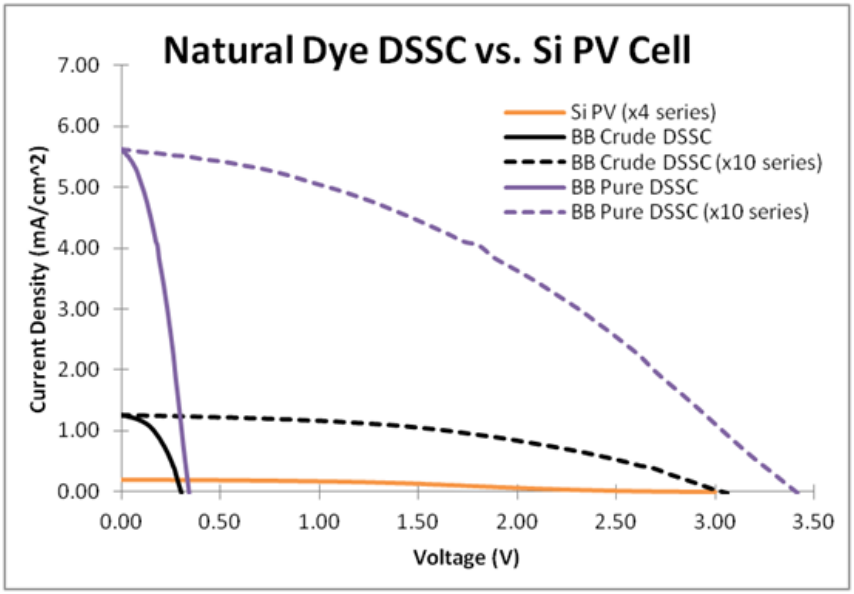

Figure 10. Natural dye DSSC vs. silicon photovoltaic cell.

4. Conclusions

Anthocyanin dyes from two different fruit sources, namely blackberry and blueberry, were successfully used in TiO_2 nanoparticle DSSC systems. Different methods were utilized for extracting anthocyanin dye molecules. This study found that mechanically extracted, blackberry-based anthocyanin DSSCs gave a photovoltaic output while the blueberry-based DSSCs did not. This can be contributed to the fact that much of the anthocyanin contained in blueberries is found in the blueberry skin, which could not be completely extracted simply through pulverization.

Chemically extracted, blackberry-based DSSCs were also found to produce current results which were almost 5× greater than the current produced by the mechanically extracted anthocyanin DSSCs. This can be attributed to the uniformity of the purified anthocyanin dye. The purified blueberry-based DSSCs were also found to produce greater current compared to the purified blackberry-based DSSCs. This could be due to the fact that the chemical extraction for blueberries may have produced a more concentrated blueberry-anthocyanin solution. Further research into the concentrations of the purified anthocyanin extracts will be determined in the future.

It was also found that these DSSCs could potentially be a natural alternative to silicon solar cells. Work is in progress to produce an arrayed natural DSSC on flexible FTO substrates to achieve optimal *I*sc and *V*oc levels for low-power applications. Future studies will also include additional fruits as anthocyanin sources to determine their relative merits for application in green chemistry-based DSSCs.

5. References

1. O'Regan, B.; Grätzel, M. A Low-Cost, High-Efficiency Solar Cell Based on Dye Sensitized Colloidal TiO2 Films. *Nature* **1991**, *353*, 737–740.
2. Shankar, K.; Bandara, J.; Paulose, M.; Wietasch, H.; Varghese, O.; Mor, G.; LaTempa, T.; Thelakkat, M.; Grimes, C. Highly Efficient Solar Cells using TiO2 Nanotube Arrays Sensitized with a Donor-Antenna Dye. *Nano Letters* **2008**, *8*, 1654–1659.
3. Zhou, H.; Wu, L.; Gao, Y.; Ma, T. Dye-Sensitized Solar Cells Using 20 Natural Dyes as Sensitizers. *Journal of Photochemistry and Photobiology A Chemistry* **2011**, *219*, 188–194.
4. Fuleki, T.; Francis, F. J. Quantitative Methods for Anthocyanins. Determination of Individual Anthocyanins in Cranberry and Cranberry Products. *Journal of Food Science* **1968**, *33*, 471–478.
5. Hao, S.; Wu, J.; Huang, Y.; Lin, J. Natural Dyes as Photosensitizers for Dye-Sensitized Solar Cell. *Solar Energy* **2006**, *80*, 209–214.
6. Park, N. G.; Lagemaat, J.; Frank, A. Comparison of Dye-Sensitized Rutile- and Anatase Based TiO2 Solar Cells. *The Journal of Physical Chemistry B* **2000**, *104*, 8989–8994.
7. Smestad, G. P.; Grätzel, M. Demonstrating Electron Transfer and Nanotechnology: A Natural Dye-Sensitized Nanocrystalline Energy Converter. *Journal of Chemical Education* **1998**, *75*, 752–756.

List of Symbols, Abbreviations, and Acronyms

DSSCs	dye-sensitized solar cells
FTO	fluorine tin oxide
HOMO	highest occupied molecular orbitals
*I*sc	short circuit current
I-V	current-voltage
NP	nanoparticle
TiO_2	titanium dioxide
*V*oc	open circuit voltage

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